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Chronoamperometry Study Of The Inhibition Of Groundwater Scaling Deposits In Fourchi

Rayane Menzri[a], Samira Ghizellaoui[a,]a*

[a]Département de Chimie, Université de Mentouri de Constantine, Route de Ain el Bey 25000 Algérie.

Abstract

Fourchi groundwater supply for the city of Aïn M 'lila drinking water are very hard (76 °F) because they are loaded into tartar, which consists mainly of calcium carbonate and its deposition in various industrial plants and networks distribution of water lead to many problems of a technical and economic as:

-Desactivation of detergents and soaps by forming complexes with calcium ions.

- Partial or total blockage of the pipes with lower river flows.

-Lower heat transfer in the case of boilers.

In this study we used the electrochemical method for accelerated scaling is based on the reduction of dissolved oxygen at a negative potential fixed (-1 V) to study the effect of temperature and the effect of concentration of inhibitors K_3PO_4 and NaOH on power encrusting water. The study of the accelerated scaling curve has shown that these waters are scaling times of 20.3 min at 20 °C and 7.3 min at 50 °C. The effect of inhibitor is pronounced characterized by obtaining a straight line from 3.5 mg/L K_3PO_4, 150 mg/L of NaOH at 20 °C. For tests at 50 °C showed that the effect of temperature significantly reduces the time scaling at 20 °C.

Keywords: Calcium Carbonate; Scaling accelerated; Inhibition; K_3PO_4; NaOH.

1. Introduction:

Fourchi groundwater supply for the city of Aïn M 'lila come from limestone and therefore they are supersaturated with calcium salts which give rise to deposits encrusting causing subsequent reductions in flow due to the increase in the thickness of the layer of scale in the flow of these waters. To do this, a number of chemical treatments (GABRIELLI et al. (1996) [1], VASINA et GUSEVA (1999) [2], LEDION et al. (2002) [3], PIN LIN et SINGER (2006) [4]), electrochemical (KHALIL et al. (1992) [5], LEROY et al. (1993) [6], ROSSET et al. (1997) [7], KETRANE et al. (2009) [8], MARTINOD et al. (2009) [9] were used to limit its precipitation.

Some chemical inhibitors (K_3PO_4, NaOH ...) can be added to block the germination and growth of crystals of calcium carbonate.

In this study, we evaluated the physico-chemical hard water Fourchi, then we studied the effect of temperature and concentration of inhibitors K_3PO_4 and NaOH to the furring Fourchi water by electrochemically method.

* Corresponding author. Tel.: 00.213.31.81.88.16 ; fax : 00.213.31.81.88.16.

E-mail address: *gsamira@yahoo.com*.

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2. Materials and methods:

The technique of accelerated scaling has been development by Ledion et al. (1985) [10]. Its principle is to coat calcium carbonate a metal surface at a potential negative fixed (-1 V) compared to a reference electrode in saturated KCl.

The electrochemical method causes the formation of a controlled deposition of calcium carbonate in an indicator electrode for the reduction of dissolved oxygen under conditions of convective diffusion, by:

$$O_2 + 4e^- + 2H_2O \longrightarrow 4\,OH^-$$

$$2\,H_2O + 2e^- \longrightarrow 2\,OH^- + H_2\,(g)$$

He settled a pH gradient between the electrode surface where it reaches higher values due to the generation of OH^- ions and resulting in formation of CO_3^{2-} according to the reaction:

$$HCO_3^- + OH^- \longrightarrow CO_3^{2-} + H_2O$$

Hydroxide ions formed precipitate calcium carbonate on the surface of t he electrode, forming a compact deposit. The setup used in the Fig. 1 was developed by Ledion et al. (1985) [10] and used at the Ecole Nationale Superieure des Arts et Métiers. It should be noted that the test conditions have been improved by Ledion (1994) [11] by following the steps in order to have good sensitivity and good reproducibility with a fixed electrode and this, to overcome the problems related to the use of a rotating electrode. The main operations are:

1) The polishing of the working electrode with sandpaper (p 400).
2) The manual brushing of the electrode with a brush made of mild steel.
3) The positioning of the three electrodes in the cover (the working electrode should be as close as possible to the platinum electrode and at a constant distance).
4) The filling of the mother cell of 500 ml and the desired temperature for the test in a water bath with slight agitation.
5) Registration of the curve I = f (t) and determining the time of conventional scaling t_E.
6) The cleaning by brushing between each test.

Fig. 1. Experimental setup.
1- Potensiostat-galvanostat; 2- Voltmeter to monitor the potential
3- Glass beaker of 600 ml; 4- Magnetic stirrer
5- Bar magnet; 6-Reference electrode Calomel saturated KCl
7- Platinum electrode; 8- Sample: steel pelle XC10 (1,003 cm^2) embedded in an inert resin.
9- Plotter; 10- Cover electrode holder; 11- Cap sample holder

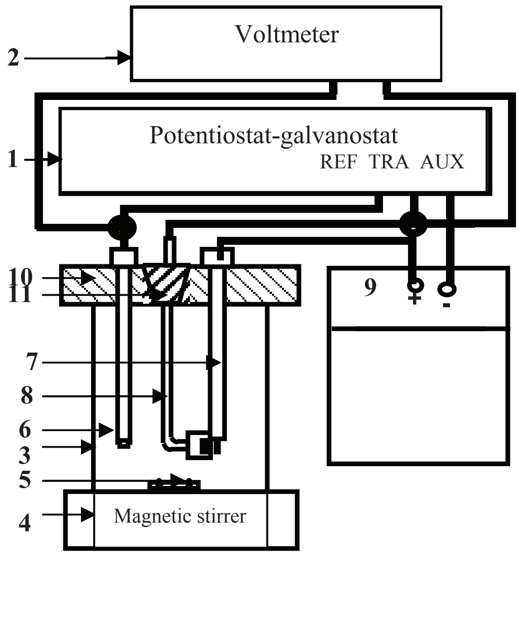

Figure 1: Experimental setup.

3. Results and discussion:
3. 1. Physico-chemical characteristics of water Fourchi:

The analytical results obtained on the physico-chemical groundwater of Fourchi are brought in Table (1).

Table 1: Water Analysis of Fourchi

The parameters	Water of Fourchi	OMS standards
T °C	20	25
pH	7.4	6.5-8.5
CE mS/cm	1.09	1.25
O_2 dissous mg/L	9. 3	-
HCO^-_3 mg/L	584	200
TH mg/L $CaCO_3$	760	350
Ca^{2+} mg/L	146	100
Mg^{2+} mg/L	95	50
Cl^- mg/L	500	250
SO_4^{2-} mg/L	222	400
NO_3^- mg/L	33	50

It should be noted that the water in Fourchi is mineralized and naturally rich in calcium and magnesium. So it is of high hardness.

3. 2. Accelerated testing of scaling the raw water of Fourchi :

The shape of the curve I = f (t) allowed us to determine the time of scaling, the latter is defined by the intersection of the tangent at the inflection point of the curve Chronoamperometric with the time axis. From this time we can define the scaling index (Ie). Chronoamperometric curve of the raw water Fourchi carried out at 20 °C is shown in Figure 2.

We define the scaling index (Ie) by the relation:

$$I_e = 1000 / t_E$$

This index is used to classify waters as follows:

Extremely scale-forming water: $100 < I_e < 1000$
Very scale-forming water: $15 < I_e < 100$
Medium scale-forming water: $5 < I_e < 15$
Slightly water scale-forming: $0.5 < I_e < 5$

The calculation of Ie gave a value of 49.26 min^{-1} of Fourchi. So, this water is in the field (15 <Ie <100) very scale-forming water.

Initially, the current has a high value and then decreases with time as the deposit of calcium carbonate formed is isolated and creates a voltage to the reduction of dissolved oxygen.

In the vicinity of the electrode [1] observed an increase in pH is due to the generation of OH^- ions then there was a slight decrease in pH indicating a precipitation of calcium carbonate on the surface of the electrode the act of germination and growth of crystals.

You should not wear the electrode potential too negative when the water itself would be reduced because the hydrogen evolution accompanying disrupt the deposition of calcium carbonate, $CaCO_3$ particles can even be detached by the bubbles of hydrogen [12].

It is to be observed in the raw water Fourchi that shape of the curve corresponds to a scale-forming water with t_E = 20.3 min and a residual current of 26.99 µA/cm². This corresponds to a compact precipitate of $CaCO_3$.

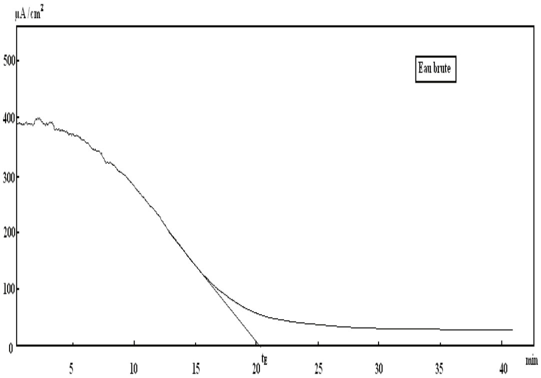

Fig. 2. Chronoamperometric curve of Fourchi at 20 °C.

3. 3. Influence of temperature on the waters of Fourchi:

To check the influence of temperature on the waters of Fourchi, several tests were carried out by considering temperatures of 20 °C to 50 °C and chronoamperometric curves are shown in Fig 3.

It is observed that when the temperature is raised from 20 °C to 50 °C, the t_E decreases from 20.3 min to 7.3 min (Table 2) confirming the favourable rôle of temperature on the calcium deposits [13] because the rise in temperature reduces the solubility of oxygen by accelerating the reduction reaction [14]. When the temperature increases the time scaling becomes shorter and the water becomes scale-forming. For low values of the residual current, the deposit is insulation.

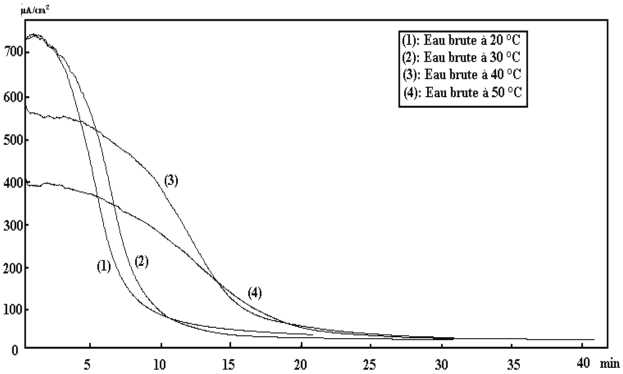

Fig. 3. Chronoamperometric curves of the raw water of Fourchi in different temperatures.

Table 2. Evolution of t_E in Fourchi water with temperature.

Work temperature (°C)	t_E (min)	I_R (μA/cm²)
20	20.3	21.16
30	11.2	29.86
40	6.7	27.83
50	5.3	26.07

4. Inhibition of calcification by chronoamperometry:

To prevent the formation of tartar, several electrochemical processes can be applied.

Products (K_3PO_4, NaOH) were used in tests of scaling accelerated. For such concentrations see Table (3).

Table 3. Range of concentrations (K_3PO_4, NaOH) used for electrochemical water softening of Fourchi.

Concentration range used (mg/L)	
K_3PO_4	NaOH
0.2	0.3
0.3	0.4
0.4	1
1	1.5
1.5	100
2	150
2.5	-
3	-
3.5	-

4. 1. Inhibition of calcification by K_3PO_4:

It highlighted the phenomenon of inhibition of calcification by the use of K_3PO_4 by determining the threshold effect, which is 0.2 mg/L of Fourchi.

Increasing concentrations (0.2, 0.3, 0.4, 1, 1.5, 2, 2.5, 3) mg/L potassium phosphate (K_3PO_4) were added to the water Fourchi at 20 °C.

The treated water has been subject to assessment by chronoamperometry.

The review shows chronoamperometric curves in the presence of K_3PO_4 time scaling increases with the concentration and the current decreases to tend to the residual current, Fig. 4 and Table 4.

This drop in intensity is not the result of deposition of $CaCO_3$ on the electrode but the precipitation of potassium phosphate (K_3PO_4) in alkaline medium (pH approaches 8) according to the reaction:

$$3HCO_3^- + 2K_3PO_4 + 3Ca^{2+} + 3OH^- \longrightarrow Ca_3(PO_4)_2\downarrow + 3\,K_2CO_3 + 3H_2O$$

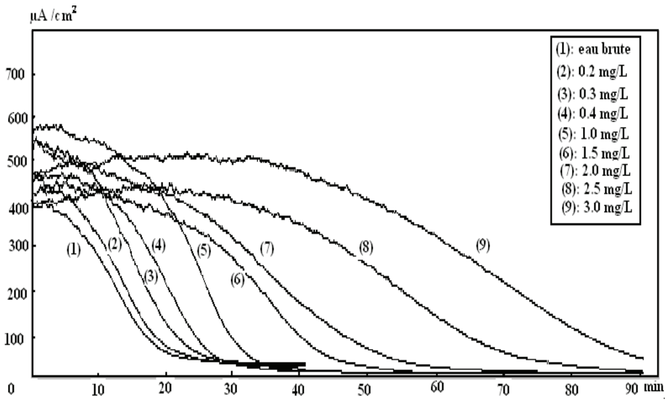

Fig. 4. chronoamperometric curves of Fourchi for the addition of different concentrations of K_3PO_4 at 20 °C.

Table 4. Evolution of t_E in Fourchi water treated with the concentration of K_3PO_4

K_3PO_4 (mg/L)	t_E (min)
0	20.3
0.2	22.3
0.3	24.2
0.4	26.6
1	33
1.5	46
2	56.5
2.5	78.5
3	89.7
3.5	∞

Calcium is precipitated as calcium phosphate. The time scaling becomes infinite at a concentration of 3.5 mg/L when inhibits the water of Fourchi, see Fig 5. The shape of the curve becomes a straight chronoamperometric. The residual current increases with the concentration of K_3PO_4 because there is no scaling.

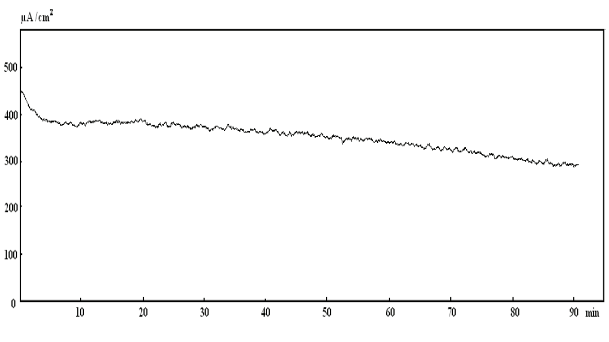

Fig. 5. Chronoamperometric curve of Fourchi for an addition of 3.5 mg/L of K_3PO_4 at 20 °C.

4. 2. Inhibition of calcification by NaOH:

For the tests performed in the presence of NaOH. Chronoamperometric curves obtained for additions of increasing concentrations (0.3, 0.4, 1, 1.5, 100) mg/L at water of Fourchi are represented in Fig 6 and the precipitation reaction leads to calcium carbonate according to this reaction:

$$Ca^{2+} + 2HCO_3^- + 2Na^+ + 2OH^- \longrightarrow CaCO_3 \downarrow + Na_2CO_3 + 2H_2O$$

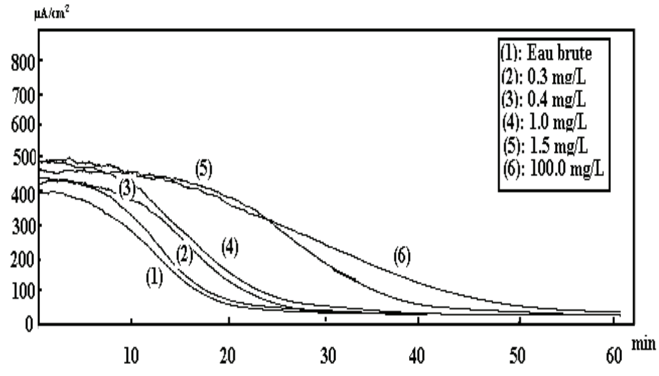

Fig. 6. Chronoamperometric curves of Fourchi for the addition of different concentrations of NaOH at 20 °C.

The time scaling increases with the concentration of NaOH added, Table 5.

Table 5. Evolution of t_E in Fourchi water treated with the concentration of NaOH

NaOH (mg/L)	t_E (min)
0	20.3
0.3	22
0.4	24.2
1	28.8
1.5	40
100	51
150	∞

It is observed that the effect of the inhibitor was started from 0.3 mg/L. The time scaling is practically infinite for 150 mg/L addition of NaOH. See Fig 7.

Calcium carbonate does not adhere to the electrode.

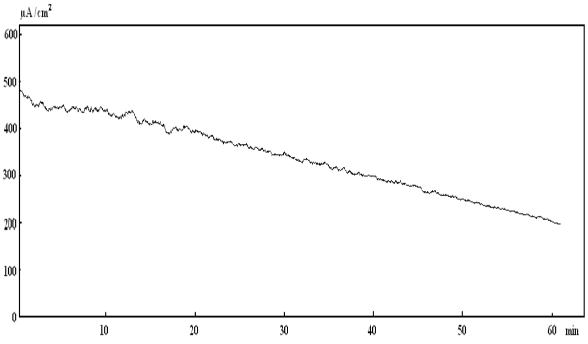

Fig. 7. Chronoamperometric curve of Fourchi for an addition of 150 mg/L of NaOH at 20 °C.

As the residual current measure the rate at which dissolved oxygen is reduced to a mild steel electrode covered with a deposit of calcium carbonate. More the deposit is less compact and adherent oxygen can diffuse through the insulating film and the residual current is low [15].

The (Table, 5) above confirms that the deposition of calcium carbonate continues to oppose the reduction of oxygen from a concentration of 0.3 mg/L of NaOH at Fourchi.

4. 3. Effect of concentration of K_3PO_4 and the NaOH on water of Fourchi treated at 50 ºC:

Chronoamperometric curves obtained for additions of increasing concentrations of K_3PO_4 and NaOH are shown in Figures (8 and 9). These curves are given at 50 ºC.

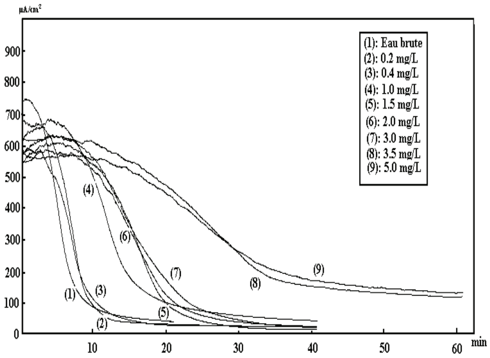

Fig. 8. Chronoamperometric curves of Fourchi for the addition of different concentrations of K_3PO_4 at 50 °C.

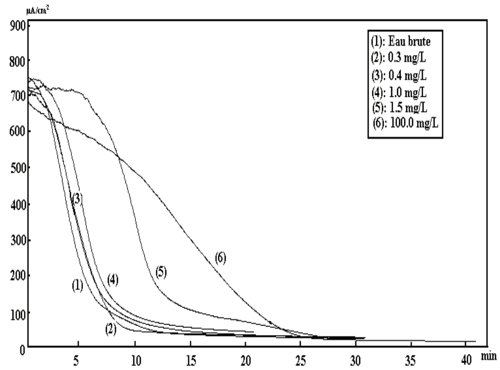

Fig. 9.Chronoamperometric curves of Fourchi for the addition of different concentrations of NaOH at 50 °C.

For tests in the presence of K_3PO_4 and NaOH Tables (6 and 7) showed that the effect of temperature (50 °C) significantly reduced t_E over 20 ºC. See previous Tables (4 and 5).

Table 6. Evolution of t_E in Fourchi water treated at 50°C with the concentration of K_3PO_4

K_3PO_4 (mg/L)	t_E (min)
0	20.3
0.2	8.2
0.4	10.4
1	18.4
1.5	21
2	23.4
3	26.2
3.5	41.5
5	∞

Table 7: Evolution of t_E in Fourchi water treated at 50°C with the concentration of NaOH.

NaOH (mg/L)	t_E (min)
0	20.3
0.3	7.1
0.4	7.7
1	8
1.5	8.5
100	23

5 .Conclusion:

Using the method Chronoamperometric (accelerated scaling) revealed that water of Fourchi has a high furring and the addition of inhibitors (K_3PO_4 and NaOH) at different concentrations may provide effective softening in these waters, which will have the effect, the significant increase in the time scaling for the waters.

It should be noted that the time scaling increases with the concentration of the inhibitors.

In addition, the inhibitory effect of K_3PO_4 occurs from 0.2 mg/L.

But, for the use of NaOH, the effect is remarkable from 0.3 mg/L.

We noted that total inhibition of the scaling is obtained for an addition of 3.5 mg/L K_3PO_4 or an addition of 150 mg/L of NaOH. This leads to a scaling time (t_E) infinite and calcium carbonate does not adhere to the working electrode.

For tests at 50 ºC in the presence of K_3PO_4 and NaOH showed that the effect of temperature significantly reduces the time scaling compared to 20 ºC.

In addition, it should be noted when the temperature increases the time scaling becomes shorter and the water becomes scale-forming reaction as the reduction of oxygen is accelerated by an increase in temperature.

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